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## **(54) COATED CEMENTED CARBIDE EXCELLENT IN WEAR RESISTANCE AND ITS PRODUCTION**

### **(57)Abstract:**

**PURPOSE:** To provide obtain a new cemented carbide in which the coating layer does not cause the deterioration in toughness even by the thickening of the film and is excellent adhesion with the base metal of cemented carbide whose service life far exceeding that of the conventional coated cemented carbide is attained, and usable even under severe conditions which made impossible to use the conventional coated cemented carbide.

**CONSTITUTION:** The surface of the base metal of cemented carbide obtd. by sintering a hard phase essentially consisting of WC by a bonding phase essentially consisting of Co is applied with a WC film formed by a thermal CVD method using the fluoride of W and a ceramic layer provided on the WC film, and cobalt is cemented from the base metal of the cemented carbide into the WC film over a depth of &ge;5&mu;m to produce the objective cemented carbide.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to the covered cemented carbide suitable for using it as antifriction parts besides a cutting tool metallurgy type, and a structural material which gave the wear-resistant ceramic coat to the front face, and its manufacture method.

[0002]

[Description of the Prior Art] Cemented carbide is a compound alloy which sintered the hard phase which makes a tungsten carbide (alpha-WC) a principal component by the binder phase which makes cobalt (Co) a principal component, and is utilized in the various fixtures which need the abrasion resistance of not only a cutting tool metallurgy type but mechanical seal, a dice, etc. or the machine part, and the field broad as a structural material.

[0003] Moreover, recently in connection with the environment used becoming still severer, the so-called covered cemented carbide in which the wear-resistant ceramic coat was formed on the front face of cemented carbide is widely used using PVD (a physical vapor deposition or the physical gaseous-phase depositing method), such as CVD (a chemical vapor deposition or the chemistry gaseous-phase depositing method), such as heat CVD, a plasma CVD method, and MO-CVD that uses an organometallic compound as a raw material, and a vacuum deposition method, the ion plating method, the sputtering method.

[0004] As an example of this ceramic coat, the titanium carbide (TiC), the titanium nitride (TiN), the alumina (aluminum 2O<sub>3</sub>), etc. are mainly used. By preparing these ceramic coats in a monolayer or a double layer on the surface of cemented carbide, it is known well the abrasion resistance of cemented carbide not only improves, but that it can prevent the reaction of \*\*-ed material and cemented carbide when using it as a cutting tool, and it can aim at improvement in a tool life as a result.

[0005] However, when the injury on an actual cutting tool metallurgy type etc. is investigated in detail, the case where the depth of an abrasion is over the thickness of a ceramic coat greatly is almost the case. That is, wear is only the first stage very much, and that the ceramic coat demonstrates the abrasion resistance as expected is suppressing advance of wear of the edge of a ceramic coat, after the wear depth exceeds the thickness of a ceramic coat. Therefore, after it wears a ceramic coat out and a cemented carbide base material is exposed, the abrasion resistance of a covered-cemented-carbide tool is influenced by the abrasion resistance which cemented carbide itself has.

[0006] Although it is expected from such a viewpoint that the abrasion resistance of a covered-cemented-carbide tool will improve if thickness of a ceramic coat is thickened, it is the present condition that the covered cemented carbide which toughness will fall if the brittleness of a ceramic, therefore the thickness of a ceramic coat are set to 10 micrometers or more in fact, shortening the life of a covered-cemented-carbide tool on the contrary is known, and has the ceramic coat of the thickness beyond this is not put in practical use. That is, it is thought that tensile stress remains, this makes a ceramic coat generate a crack, and the ceramic of TiC, TiN, and aluminum2O<sub>3</sub> grade reduces toughness into the ceramic coat after membrane formation since the coefficient of thermal expansion is larger than the cemented carbide of a base material.

[0007] or [ then, / that it is almost the same as the cemented carbide whose coefficient of thermal expansion is a base material instead of the ceramic used conventionally /, such as TiC, ] -- or if it lowers a little, it comes out and a certain tungsten carbide (WC) is used as an enveloping layer, in WC coat after membrane formation, the residual stress by thermal stress will hardly arise, or it will only be that some compressive stress remains Therefore, even if it forms WC coat in a cemented carbide front face, thick-film-ization is attained without not producing a crack and reducing the toughness of WC coat, and moreover, since a binder phase is not included and the degree of hardness is higher than cemented carbide, WC coat can expect the wear-resistant improvement in a covered-cemented-carbide tool.

[0008] In accordance with this idea, the surface coating tool parts in which the enveloping layer of the tungsten (W) which set the diameter of crystal grain to 1 micrometer or less by carrying out specified quantity content of a fluorine or the chlorine as an outermost layer of drum, or tungsten carbide (WC) was formed on the front face of tool parts are proposed by JP,59-39242,B and JP,61-46550,B. However, WC coat has come to acquire the tool life which should be satisfied [ with the bottom of a severe condition ] of the diameter of crystal grain since cemented carbide cannot be endured in respect of toughness as 1 micrometer or less and there is a problem also about the adhesion of WC coat and a tool base material.

[0009]

[Problem(s) to be Solved by the Invention] In view of this conventional situation, an enveloping layer does not cause the fall of toughness by thick-film-ization, either, and this invention is excellent in adhesion with a cemented carbide base material, and it

not only can attain the life far exceeding the conventional covered cemented carbide, but aims at the usable thing for which a new covered cemented carbide is offered under the severe condition which has not been used by the conventional covered cemented carbide.

[0010]

[Means for Solving the Problem] The covered cemented carbide which this invention offers in order to attain the above-mentioned purpose is equipped with the ceramic coat which was [ cobalt ] excellent in the abrasion resistance which prepared on the cemented carbide base material sintered by the binder phase which considers as a principal component, the tungsten-carbide coat formed in the front face, and the tungsten-carbide coat in the hard phase which makes a tungsten carbide a principal component, and is characterized by for the cobalt which is a binder phase to carry out diffusion osmosis covering a depth of 5 micrometers or more into a tungsten-carbide coat from the cemented-carbide base material.

[0011] In the manufacture method of the above-mentioned covered cemented carbide, a tungsten-carbide coat is formed in the front face of a cemented carbide base material by the heat CVD using the fluoride, the hydrocarbon, and hydrogen of a tungsten as reactant gas at the base material temperature of 500-900 degrees C of cemented carbide, and a ceramic coat is formed at the base material temperature of 450-1200 degrees C on this tungsten-carbide coat after that by CVD, such as heat CVD, a plasma CVD method, and MO-CVD, and PVD, such as the ion plating method.

[0012] In order to obtain diffusion osmosis of cobalt with a depth of 5 micrometers or more from a cemented carbide base material in a tungsten-carbide coat in that case, it is required to heat the cemented carbide base material which has a tungsten-carbide coat at 950-1200 degrees C for 5 hours or more. In order to fulfill this heating condition, [ whether in advance of formation of a ceramic coat homogenizing of 5 hours or more is performed at 950-1200 degrees C after formation of a ceramic coat, and ] Or although what is necessary is just to form membranes on the conditions of 5 hours or more using the heat history at the time of membrane formation of a ceramic coat the base material temperature of 950-1200 degrees C, and membrane formation time, both heating at the time of membrane formation of homogenizing and a ceramic coat may attain the heating conditions of 5 hours or more at 950-1200 degrees C in total.

[0013]

[Function] The ceramic coat used for the covered cemented carbide from the former in this invention, for example, as a ground layer of TiC, TiN, Ti (CN), HfN, HfC and Hf (CN), ZrN, ZrC and Zr (CN), TiBN, aluminum<sub>2</sub>O<sub>3</sub>, HfO<sub>2</sub>, and ZrO<sub>2</sub> grade Using the thick film of the tungsten carbide (WC) which is one sort of a ceramic by carrying out diffusion osmosis of the cobalt which is the binder phase of cemented carbide further positively covering a depth of 5 micrometers or more into WC coat from a base material In spite of thick-film-izing of an enveloping layer, the toughness of WC coat improves, and it was able to become clear and have that adhesion with about [ hardly happening ] and a base material is also improved remarkably, and the fall of a degree of hardness was also able to raise the abrasion resistance of a covered cemented carbide remarkably.

[0014] Although the thickness of WC coat is influenced by the environment used as a cutting tool metallurgy type, a fixture, etc., a life, a dimensional accuracy which were set up, etc., it is desirable that it is generally the range of 5-100 micrometers. It is because a manufacturing cost will increase in less than 5 micrometers in order the toughness of a covered cemented carbide not only to fall, but for WC coat to become comparatively weak and for membrane formation to take a long time, if the effect of wear-resistant improvement according [ thickness ] to formation of WC coat and diffusion of Co is hardly seen and 100 micrometers is exceeded.

[0015] PVD, such as heat CVD using the chloride and carbonyl of a tungsten as the formation method of this WC coat, and the ion plating method using the metal tungsten, the sputtering method, can be considered. However, although 10micrometers [/o'clock ] or more membrane formation speed is economically required of this invention in order to obtain comparatively thick WC coat, since it is difficult to raise the speed of supply of the tungsten which is a refractory metal in PVD, membrane formation speed is very slow in at most 1micrometer/[ o'clock and ]. Moreover, for a low reason, in the conventional heat CVD, the chloride of a tungsten and the vapor pressure of a carbonyl which are a raw material are difficult for obtaining 5micrometers [/o'clock ] or more membrane formation speed.

[0016] Then, according to the heat CVD using the fluoride (for example, WF<sub>6</sub>) of a tungsten the result of examination, high-speed supply of fluoride gas is possible, and it turns out by making this react with the hydrocarbon gas of C<sub>3</sub>H<sub>8</sub> or C<sub>6</sub>H<sub>6</sub> grade, and hydrogen gas that WC coat can be formed extremely at high speed. However, the carbon content in WC coat from which it is obtained [ that base material temperature of cemented carbide cannot attain 10micrometers //o'clock / or more membrane formation speed at less than 500 degrees C and ] is low, and since a coat composition phase turns into a single phase of WWW consortium, only very weak WC coat is obtained. On the contrary, if base material temperature exceeds 900 degrees C, material gas will react in a gaseous phase and only a powdered product will be obtained.

[0017] Next, the ceramic coat of TiC, TiN, Ti (CN), HfN, HfC and Hf (CN), ZrN, ZrC and Zr (CN), TiBN, aluminum<sub>2</sub>O<sub>3</sub>, HfO<sub>2</sub>, and ZrO<sub>2</sub> grade is covered on this WC coat. As the formation method, although CVD, such as heat CVD, a plasma CVD method, and MO-CVD, and PVD, such as the ion plating method, can be used, it is necessary to make base material temperature into 450-1200 degrees C. The base material temperature of the reason is because change arises at less than 450 degrees C in the organization of the cemented carbide which is a base material when there is risk of a coat exfoliating without the adhesion of a ceramic coat being low and being able to bear the heat history in a back process and 1200 degrees C is exceeded on the other hand and the performance of original cemented carbide is spoiled.

[0018] Furthermore, in this invention, although Co which makes the binder phase of cemented carbide required carrying out depth diffusion osmosis of 5 micrometers or more into WC coat from the base material, it became clear that for that 5 hours or

more need to be heat-treated of 950-1200 degrees C. If Co is not spread [ temperature ] by less than 950 degrees C or heating time in depth of 5 micrometers or more in WC coat in less than 5 hours and temperature exceeds 1200 degrees C, change will arise in the organization of the cemented carbide which is a base material, and the performance of original cemented carbide will be spoiled.

[0019] As the heating method for obtaining this diffusion osmosis of Co \*\* Although there is the method of performing homogenizing of 5 hours or more at 950-1200 degrees C after formation of a ceramic coat in advance of formation of a ceramic coat, or forming membranes over 5 hours or more using the heat history at the time of membrane formation of \*\* ceramic coat at the base material temperature of 950-1200 degrees C \*\* You may make it heating [ of 5 hours or more ] fill with the above-mentioned 950-1200 degrees C [ both heating at the time of membrane formation of the above-mentioned homogenizing and a ceramic coat ].

[0020] Although respectively different membrane formation equipment and a respectively different heat treating furnace may perform each process of formation of formation of the above WC coat, homogenizing, and a ceramic coat, processing continuously is desirable, without exposing to the atmosphere within the same membrane formation equipment, if it can do. It is because there is a possibility that it may be polluted by oxygen and the moisture in the atmosphere and a front face may have a bad influence on processing of a back process when the atmosphere is touched, in case a processed material is movement. Moreover, if separate equipment is used for every process, make-ready times, such as movement to equipment from equipment, will occur too much, and will also become the cause of raising a manufacturing cost.

[0021] However, since formation of WC coat is based on CVD and the same equipment cannot necessarily be used, when forming a ceramic coat by PVD, such as the ion plating method, after performing homogenizing within the membrane formation equipment of CVD if needed [ membrane formation and if needed ] for WC coat, taking out a base material in the atmosphere and washing, it is desirable to form a \*\*\*\*\* ceramic coat in the membrane formation equipment of PVD.

[0022]

[Example]

A cemented carbide tool with the composition which consists of Example 1WC:85 % of the weight, Co:10 % of the weight, and TiC:5 % of the weight is installed in the interior of the membrane formation equipment made from a heat-resistant alloy. by the heat CVD of the following reaction condition (1); WF6 1 mol %C6H6 5 mol %H2 10 mol %(2) reactant-gas flow rate; A 1.6l. part (3) mother for / Material \*\* Degree ; 800-degree-C (4) \*\* WC coat was formed in the front face for between s; 30 minutes at the time of reactant gas condition \*\* .

[0023] It has checked that obtained WC coat was constituted from alpha-WC by the X diffraction. Moreover, the thickness of WC coat is 7 micrometers and it turns out that membrane formation speed is 14micrometers/o'clock. When the cross-section degree of hardness of this WC coat was measured with the Knoop hardness plan (50g of loads), about 2400kg /of values of 2 was acquired mm as a degree of hardness of WC coat. Furthermore, when the adhesion intensity of WC coat was scratched and having been evaluated using the formula adhesion on-the-strength measurement machine, ablation of a coat arose in 25 Ns (Newton).

[0024] By the usual heat CVD, this WC covered-cemented-carbide tool was again installed in the interior of the same membrane formation equipment, the basis with a base material temperature of 980 degrees C took reaction-time 3 hours, the TiC coat was formed, further, on it, the basis with a base material temperature of 1000 degrees C took reaction-time 5 hours, and 2Oaluminum3 coat was formed (example 1 of this invention). The photograph of the metal texture of the

covered-cemented-carbide tool cross section of the acquired example 1 of this invention was shown in drawing 1 . By this cross-section observation, the sum total thickness of a TiC coat and 2Oaluminum3 coat is 6 micrometers, and it has checked that Co was carrying out diffusion osmosis by about 7-micrometer Fukashi into WC coat from the base material.

[0025] Moreover, when the adhesion intensity of a coat was measured like the above, it turns out that the ablation by the interface of WC coat and a TiC coat is not accepted, but the ablation by the interface of WC coat and a base material is generated in 95 Ns, and adhesion intensity is improving farther than the case of only WC coat. Furthermore, the cross-section degree of hardness of the thickness direction of the covered-cemented-carbide tool measured with the same Knoop hardness plan as the above was shown in drawing 2 .

[0026] For comparison, the plasma CVD method was used for the front face of WC covered-cemented-carbide tool which formed WC coat like the above, and the TiC coat and 2Oaluminum3 coat were formed in it at the base material temperature of 900 degrees C (example 1 of comparison). When the cross section of the covered-cemented-carbide tool of the acquired example 1 of comparison was observed, the sum total thickness of a TiC coat and 2Oaluminum3 coat is 5 micrometers, and diffusion of Co was not accepted at all between the base material and WC coat. Moreover, when the adhesion intensity of a coat was measured like the above, the ablation by the interface of a base material and WC coat was started by 30 Ns, and adhesion intensity was very low compared with the example 1 of this invention.

[0027] After annealing WC covered-cemented-carbide tool which formed WC coat (7 micrometers of thickness) like the example 2 above-mentioned example 1 at 1050 degrees C for 5 hours, the following ceramic coat was formed on this WC coat, and the covered-cemented-carbide tool of the examples 2-5 of this invention was obtained.;

Example [ of This invention ] 2: The ceramic coat of 6 micrometers of sum total thickness which carried out the laminating of a TiC coat, a TiBN coat, and the 2Oaluminum3 coat (plasma CVD method; base material temperature of 900 degrees C)

Example [ of This invention ] 3: The ceramic coat of 7 micrometers of sum total thickness which carried out the laminating of HfO2 coat and the 2Oaluminum3 coat (MO- using the metal alkoxide CVD; base material temperature of 700 degrees C)

Example [ of This invention ] 4: The ceramic coat of 6 micrometers of sum total thickness which carried out the laminating of a

HfN coat and the HfC coat (ion plating method; base material temperature of 600 degrees C)

Example [ of This invention ] 5: The ceramic coat of 7 micrometers of sum total thickness which carried out the laminating of a ZrN coat, Zr (CN) coat, and the ZrC coat (ion plating method; base material temperature of 600 degrees C)

[0028] When the cross section of each covered-cemented-carbide tool of the examples 2-5 of this invention is observed, Co has diffused all covering a depth of 6 micrometers in WC coat of 7 micrometers of thickness from the base material. The adhesion intensity of WC coat has improved by 95 Ns and the example 3 of this invention in the example 2 of this invention more sharply than the adhesion intensity of 25 Ns WC coat independent [ this ] for which asked for by 92 Ns in 93 Ns and the example 4 of this invention, and each asked in the example 1 with 94 Ns by the example 5 of this invention.

[0029] For comparison, after annealing WC covered-cemented-carbide tool in which the same WC coat (7 micrometers of thickness) was formed, at 1000 degrees C for 2 hours, the ceramic coat of 6 micrometers of sum total thickness which carried out the laminating of a TiC coat, a TiBN coat, and the 2Oaluminum3 coat was formed at the base material temperature of 900 degrees C using the plasma CVD method on this WC coat (example 2 of comparison). When the tool cross section of this example 2 of comparison was observed, diffusion osmosis of Co from a base material to WC coat stopped at about only 2 micrometers, and the adhesion intensity of WC coat was 40Ns.

[0030] The cutting examination by the following conditions was performed about the examples 1-5 of this invention produced in the example 3 above-mentioned example 1 and the example 2, and the examples 1-2 of comparison. In addition, the cutting examination by the following conditions was similarly performed about the covered-cemented-carbide tool (example 3 of comparison) in which the TiC coat of 6 micrometers of sum total thickness and 2Oaluminum3 coat were formed on the cemented-carbide-tool front face as well as an example 1, except not forming WC coat.

[0031]

Cutting conditions: \*\*\* Material SCN435 cutting speed 250 m/min \*\*\* 0.3 mm/rev

Slitting 2mm cutting time 20 minutes [0032] The flank wear and the crater were measured by the above-mentioned cutting examination, and the result was shown in the following table 1 with Co diffusion depth of penetration to the inside of the composition of the laminating coat of each covered-cemented-carbide tool, and WC coat.;

[Table 1]

Co diffusion depth Frank Crater Tool sample Composition of a laminating coat (micrometer) Wear (mm) Example 1 of a wear (micrometer) this invention WC-TiC-aluminum 2O3 7 0.09 Example 2 of 11 this inventions WC-TiC-TiBN-aluminum 2O3 6 0.10 Example 3 of 12 this inventions WC-HfO2-aluminum 2O3 6 0.12 Example 4 of 15 this inventions WC-HfN-HfC 6 0.11 Example 5 of 14 this inventions WC-ZrN-Zr(CN)-ZrC 6 0.12 13 ratios Example of \*\* 1 WC-TiC-aluminum 2O3 0 Deficit deficit ratio \*\* Example 2 WC-TiC-TiBN-aluminum 2O3 20.32 (ablation) 20 ratios \*\* Example 3 TiC-aluminum 2O3 -0.28 In the example 2 of 25 (notes) comparison, ablation occurred in a part of coat during cutting.

[0033] As for each covered-cemented-carbide tool of the example of this invention, compared with the examples 1 and 2 of comparison with little diffusion osmosis of Co from the result of the above-mentioned table 1 to the inside of WC coat, and the example 3 of comparison which does not have WC coat, it is clear that the effect given to the wear-resistant improvement in WC coat which showed the outstanding abrasion resistance and Co diffused is remarkable. Moreover, about diffusion of Co to WC coat, it turns out that homogenizing which governs the depth of diffusion, the temperature at the time of ceramic coat membrane formation, and the history of time are important.

[0034] the cemented carbide which consists of Example 4WC:90 % of the weight and Co:10 % of the weight -- by the same method as an example 1, only membrane formation time was changed into the molding section front face of metal mold in 3 hours, and WC coat was formed in it Next, the laminating of the TiC coat +Ti(CN) coat +TiN coat was continuously carried out one by one by heat CVD within the membrane formation equipment same on this WC coat on the base material temperature of 1000 degrees C, and the conditions of membrane formation time 7 hours, and the ceramic coat was formed.

[0035] the covered cemented carbide of the acquired example of this invention -- when the cross section of metal mold was observed, it has checked that the thickness of WC coat was carrying out diffusion osmosis covering a depth of 8 micrometers into WC coat from the cemented carbide whose Co which 55 micrometers and the sum total thickness of a ceramic coat are 6 micrometers, and is the binder phase of cemented carbide is a base material

[0036] without it prepares WC coat for comparison -- the same cemented carbide -- the metal mold which formed directly the ceramic coat which comes to carry out the laminating of the TiC coat +Ti(CN) coat +TiN coat on the surface of metal mold was produced the covered cemented carbide of this example of comparison, and the above-mentioned example of this invention -- metal mold -- using -- cold forging of autoparts -- carrying out -- each -- life evaluation of metal mold was performed Consequently, the metal mold of the example of comparison was only 50,000 shots and a very short life to the metal mold of the example of this invention having reached the life in 300,000 shots. moreover -- if the damaged metal mold is observed -- the most intense metal mold of an injury -- in the corner section at a nose of cam, the cemented carbide of a ground was exposed with the metal mold of the example of comparison to WC coat having remained in the metal mold of the example of this invention

[0037] Example 5WC: WC coat of 80 micrometers of thickness was formed in the front face of the mechanical seal made from cemented carbide which consists of 90 % of the weight and Co:10 % of the weight by the same method as an example 1, and, next, homogenizing of 6 hours was given at 1200 degrees C. Then, the TiN coat of 5 micrometers of thickness was formed at the base material temperature of 700 degrees C by the plasma CVD method within the membrane formation equipment same on this WC coat.

[0038] When the cross section of the mechanical seal made from a covered cemented carbide of this example of this invention

was observed, Co which is the binder phase of cemented carbide was carrying out diffusion osmosis covering a depth of 20 micrometers into WC coat from the cemented carbide which is a base material. The mechanical seal which formed the TiN coat in the front face of the same mechanical seal made from cemented carbide directly was produced without preparing WC coat for comparison. These mechanical seal made from a covered cemented carbide was attached to the pump for slurries of the same form, and the endurance evaluation examination was carried out.

[0039] Consequently, in the example of this invention, neither seizure nor wear produced after 20,000-hour progress, but to having used it still more satisfactory, the leakage of a slurry arose for 5000 hours after the seal section, and the life was reached in the example of comparison. Although the abrasion which a TiN coat is worn out, the cemented carbide of a ground is exposed, the thing of the example of comparison does not come out, and the corrosion of cemented carbide is also observed, and exceeds a depth of 100 micrometers was also accepted when mechanical seal was investigated after the examination, the thing of the example of this invention was only worn out in Fukashi whose WC coat is 5 micrometers, and the signs of corrosion were not accepted at all.

[0040]

[Effect of the Invention] When according to this invention the fall of toughness is not caused by thick-film-ization of an enveloping layer, either, and it excels in the adhesion of an enveloping layer and a cemented carbide base material and is used as a cutting tool metallurgy type, an abrasion-resistant fixture, a machine part, a structural material, etc., it not only can attain the life far exceeding the former, but it can offer the new covered cemented carbide in which the use under the severe condition which has not been used conventionally is also possible.

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**DESCRIPTION OF DRAWINGS**

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[Brief Description of the Drawings]

[Drawing 1] It is the photograph in which the metal texture of the cross section in the covered-cemented-carbide tool of the example of this invention produced in the example 1 is shown.

[Drawing 2] It is the graph which shows the cross-section degree of hardness in the thickness direction of the covered-cemented-carbide tool of the example of this invention produced in the example 1.

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CLAIMS

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[Claim(s)]

[Claim 1] The covered cemented carbide excellent in the abrasion resistance characterized by having the ceramic coat which was [ cobalt ] excellent in the abrasion resistance which prepared on the cemented carbide base material sintered by the binder phase which considers as a principal component, the tungsten-carbide coat formed in the front face, and the tungsten-carbide coat in the hard phase which makes a tungsten carbide a principal component, and the cobalt which is a binder phase carrying out diffusion osmosis covering a depth of 5 micrometers or more into a tungsten-carbide coat from the cemented carbide base material.

[Claim 2] The covered cemented carbide excellent in abrasion resistance according to claim 1 characterized by the thickness of a tungsten-carbide coat being 5-100 micrometers.

[Claim 3] The covered cemented carbide excellent in abrasion resistance according to claim 1 or 2 characterized by the thickness being 1-15 micrometers by a ceramic coat consisting of at least one layer of TiC, TiN, Ti (CN), HfN, HfC and Hf (CN), ZrN, ZrC and Zr (CN), TiBN, aluminum<sub>2</sub>O<sub>3</sub>, HfO<sub>2</sub>, or ZrO<sub>2</sub>.

[Claim 4] The manufacture method of the covered cemented carbide excellent in the abrasion resistance characterized by forming a tungsten-carbide coat in the front face of the cemented carbide base material which sintered the hard phase which makes a tungsten carbide a principal component by the binder phase which makes cobalt a principal component by the heat CVD which used the fluoride, the hydrocarbon, and hydrogen of a tungsten as reactant gas at the base material temperature of 500-900 degrees C of a cemented carbide base material, and next forming a ceramic coat in it by CVD or PVD in 5 hours or more the base material temperature of 950-1200 degrees C,

[Claim 5] On the front face of the cemented carbide base material sintered by the binder phase which makes cobalt a principal component, the hard phase which makes a tungsten carbide a principal component A tungsten-carbide coat is formed by the heat CVD using the fluoride, the hydrocarbon, and hydrogen of a tungsten as reactant gas at the base material temperature of 500-900 degrees C of a cemented carbide base material. A ceramic coat is formed by CVD or PVD on this tungsten-carbide coat at base material 450-degree-C or more temperature of less than 950 degrees C. The manufacture method of the covered cemented carbide excellent in the abrasion resistance characterized by giving homogenizing of 5 hours or more at 950-1200 degrees C after the formation in advance of formation of the ceramic coat concerned.

[Claim 6] On the front face of the cemented carbide base material sintered by the binder phase which makes cobalt a principal component, the hard phase which makes a tungsten carbide a principal component At the base material temperature of 500-900 degrees C of a cemented carbide base material, a tungsten-carbide coat is formed by the heat CVD using the fluoride, the hydrocarbon, and hydrogen of a tungsten as reactant gas. A ceramic coat is formed by CVD or PVD at the base material temperature of 950-1200 degrees C on this tungsten-carbide coat. The manufacture method of the covered cemented carbide excellent in the abrasion resistance characterized by giving homogenizing of 5 hours or more at 950-1200 degrees C after the formation in advance of formation of the ceramic coat concerned, and making the sum total of the aforementioned homogenizing time and the membrane formation time of a ceramic coat into 5 hours or more.

[Claim 7] The manufacture method of the covered cemented carbide excellent in abrasion resistance according to claim 4 to 6 characterized by carrying out continuously, without exposing formation of a ceramic coat, or all the processes to homogenizing to the atmosphere in the same membrane formation equipment from formation of a tungsten-carbide coat.

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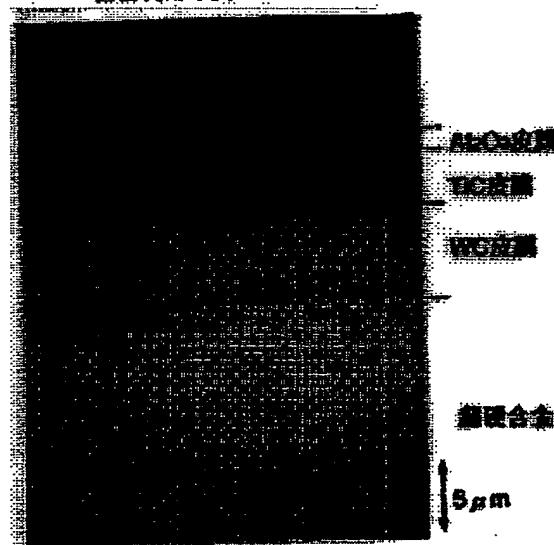
(54)【発明の名称】 耐摩耗性に優れた被覆超硬合金及びその製造方法

(57)【要約】

【目的】 被覆層が厚膜化によっても韌性の低下を招かず且つ超硬合金母材との密着性に優れ、従来の被覆超硬合金を遥かに越える寿命を達成し、従来の被覆超硬合金では使用できなかった過酷な条件下でも使用可能な、新しい被覆超硬合金を提供する。

【構成】 WCを主成分とする硬質相をCoを主成分とする結合相で焼結した超硬合金母材の表面に、Wのフッ化物を用いた熱CVD法により形成したWC皮膜と、WC皮膜上に設けたセラミックス皮膜とを備え、コバルトが超硬合金母材からWC皮膜中に深さ5μm以上にわたり拡散浸透している被覆超硬合金。

図面代替写真



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## 【特許請求の範囲】

【請求項1】 炭化タングステンを主成分とする硬質相をコバルトを主成分とする結合相で焼結した超硬合金母材と、その表面に形成した炭化タングステン皮膜と、炭化タングステン皮膜上に設けた耐摩耗性に優れたセラミック皮膜とを備え、結合相であるコバルトが超硬合金母材から炭化タングステン皮膜中に深さ $5\mu\text{m}$ 以上にわたり拡散浸透していることを特徴とする耐摩耗性に優れた被覆超硬合金。

【請求項2】 炭化タングステン皮膜の膜厚が $5\sim100\mu\text{m}$ であることを特徴とする、請求項1に記載の耐摩耗性に優れた被覆超硬合金。

【請求項3】 セラミック皮膜が、TiC、TiN、Ti(CN)、HfN、HfC、Hf(CN)、ZrN、ZrC、Zr(CN)、TiBN、Al<sub>2</sub>O<sub>3</sub>、HfO<sub>2</sub>又はZrO<sub>2</sub>の少なくとも1層からなり、その膜厚が $1\sim15\mu\text{m}$ であることを特徴とする、請求項1又は2に記載の耐摩耗性に優れた被覆超硬合金。

【請求項4】 炭化タングステンを主成分とする硬質相をコバルトを主成分とする結合相で焼結した超硬合金母材の表面に、超硬合金母材の母材温度 $500\sim900^\circ\text{C}$ にて、反応ガスとしてタングステンのフッ化物と炭化水素と水素を用いた熱CVD法により炭化タングステン皮膜を形成し、次にセラミック皮膜を母材温度 $950\sim1200^\circ\text{C}$ 及び成膜時間5時間以上にてCVD法又はPVD法により形成することを特徴とする耐摩耗性に優れた被覆超硬合金の製造方法。

【請求項5】 炭化タングステンを主成分とする硬質相をコバルトを主成分とする結合相で焼結した超硬合金母材の表面に、超硬合金母材の母材温度 $500\sim900^\circ\text{C}$ にて反応ガスとしてタングステンのフッ化物と炭化水素と水素を用いた熱CVD法により炭化タングステン皮膜を形成し、この炭化タングステン皮膜の上にセラミック皮膜を母材温度 $450^\circ\text{C}$ 以上 $950^\circ\text{C}$ 未満にてCVD法又はPVD法により形成し、当該セラミック皮膜の形成に先立って又はその形成後に $950\sim1200^\circ\text{C}$ で5時間以上の拡散焼鈍を施すことを特徴とする耐摩耗性に優れた被覆超硬合金の製造方法。

【請求項6】 炭化タングステンを主成分とする硬質相をコバルトを主成分とする結合相で焼結した超硬合金母材の表面に、超硬合金母材の母材温度 $500\sim900^\circ\text{C}$ にて、反応ガスとしてタングステンのフッ化物と炭化水素と水素を用いた熱CVD法により炭化タングステン皮膜を形成し、この炭化タングステン皮膜の上にセラミック皮膜を母材温度 $950\sim1200^\circ\text{C}$ にてCVD法又はPVD法により形成し、当該セラミック皮膜の形成に先立って又はその形成後に $950\sim1200^\circ\text{C}$ で5時間以上の拡散焼鈍を施し、前記拡散焼鈍時間とセラミック皮膜の成膜時間の合計を5時間以上とすることを特徴とする耐摩耗性に優れた被覆超硬合金の製造方法。

【請求項7】 炭化タングステン皮膜の形成からセラミック皮膜の形成又は拡散焼鈍までの全ての工程を、同一成膜装置内において大気にさらすことなく連続的に実施することを特徴とする、請求項4～6のいずれかに記載の耐摩耗性に優れた被覆超硬合金の製造方法。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】 本発明は、切削工具や金型のほか、耐摩耗部品、構造材料として使用するのに適した、

- 10 耐摩耗性のセラミック皮膜を表面に施した被覆超硬合金、及びその製造方法に関する。

## 【0002】

【従来の技術】 超硬合金は、炭化タングステン( $\alpha\text{-W C}$ )を主成分とする硬質相を、コバルト(Co)を主成分とする結合相で焼結した複合合金であり、切削工具や金型のみならず、メカニカルシールやダイス等の耐摩耗性を必要とする各種治具ないし機械部品、構造材料として幅広い分野で活用されている。

- 20 【0003】 また最近では、使用される環境が益々過酷になるのに伴い、熱CVD法、プラズマCVD法、有機金属化合物を原料とするMO-CVD法等のCVD法(化学蒸着法又は化学気相析出法)や、真空蒸着法、イオンプレーティング法、スパッタリング法等のPVD法(物理蒸着法又は物理気相析出法)を利用して、超硬合金の表面に耐摩耗性のセラミック皮膜を形成した、いわゆる被覆超硬合金が広く利用されている。

- 【0004】かかるセラミック皮膜の実例としては、主に炭化チタン(TiC)、窒化チタン(TiN)、アルミニウム(Al<sub>2</sub>O<sub>3</sub>)等が用いられている。これらのセラミック皮膜を超硬合金の表面に単層又は複層に設けることによって、超硬合金の耐摩耗性が向上するだけでなく、切削工具として使用する場合に被削材と超硬合金の反応を防止でき、結果的に工具寿命の向上が図ることは良く知られている。

- 【0005】しかし、現実の切削工具や金型等の損傷を詳しく調べると、摩耗痕の深さがセラミック皮膜の厚みを大きく越えている場合が殆どである。つまり、セラミック皮膜が期待どおりの耐摩耗性を発揮しているのは摩耗のごく初期のみであり、摩耗深さがセラミック皮膜の膜厚を越えた後は、セラミック皮膜のエッジが摩耗の進行を抑えていないに過ぎない。従って、セラミック皮膜が摩耗して超硬合金母材が露出した後は、超硬合金自身の持つ耐摩耗性によって被覆超硬合金工具の耐摩耗性が左右される。

- 【0006】この様な観点から、セラミック皮膜の膜厚を厚くすれば被覆超硬合金工具の耐摩耗性が向上することが期待されるが、実際にはセラミックの脆さ故に、セラミック皮膜の膜厚が $10\mu\text{m}$ 以上になると韌性が低下し、かえって被覆超硬合金工具の寿命を短くすることが

- 50 知られ、これ以上の膜厚のセラミック皮膜を有する被覆

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超硬合金が実用化されていない現状である。即ち、TiC、TiN、Al<sub>2</sub>O<sub>3</sub>等のセラミックは母材の超硬合金よりも熱膨張係数が大きいため、成膜後のセラミック皮膜中に引張応力が残留し、これがセラミック皮膜にクラックを生成させて韌性を低下させるものと考えられている。

【0007】そこで、TiC等の従来用いられていたセラミックの代わりに、熱膨張係数が母材である超硬合金とほぼ同じか又は若干低めである炭化タングステン(WC)を被覆層として用いれば、成膜後のWC皮膜には熱応力による残留応力が殆ど生じないか或は若干の圧縮応力が残留するのみである。従って、WC皮膜を超硬合金表面に形成してもクラックを生じることがなく、WC皮膜の韌性を低下させずに厚膜化が可能となり、しかもWC皮膜は結合相を含まないため超硬合金より硬度が高いから、被覆超硬合金工具の耐摩耗性の向上が期待できる。

【0008】この考えに沿って、特公昭59-39242号公報や特公昭61-46550号公報には、工具部品の表面に最外層として、フッ素又は塩素を所定量含有することによって結晶粒径を1μm以下としたタングステン(W)又はタングステンカーバイト(WC)の被覆層を形成した表面被覆工具部品が提案されている。しかしながら、WC皮膜は結晶粒径を1μm以下としても韌性の点で超硬合金を凌ぐことはできず、又WC皮膜と工具母材との密着性についても問題があるため、特に過酷な条件下では満足すべき工具寿命を得るに至っていない。

#### 【0009】

【発明が解決しようとする課題】本発明は、かかる従来の事情に鑑み、被覆層が厚膜化によっても韌性の低下を招かず且つ超硬合金母材との密着性に優れ、従来の被覆超硬合金を遥かに越える寿命を達成し得るのみならず、従来の被覆超硬合金では使用できなかった過酷な条件下でも使用可能な、新しい被覆超硬合金を提供することを目的とする。

#### 【0010】

【課題を解決するための手段】上記目的を達成するため、本発明が提供する被覆超硬合金は、炭化タングステンを主成分とする硬質相をコバルトを主成分とする結合相で焼結した超硬合金母材と、その表面に形成した炭化タングステン皮膜と、炭化タングステン皮膜上に設けた耐摩耗性に優れたセラミックス皮膜とを備え、結合相であるコバルトが超硬合金母材から炭化タングステン皮膜中に深さ5μm以上にわたり拡散浸透していることを特徴とする。

【0011】上記被覆超硬合金の製造方法においては、超硬合金の母材温度500~900°Cで反応ガスとしてタングステンのフッ化物と炭化水素と水素を用いた熱CVD法により、超硬合金母材の表面に炭化タングステン

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皮膜を形成し、その後この炭化タングステン皮膜の上に熱CVD法、プラズマCVD法、MO-CVD法等のCVD法や、イオンプレーティング法等のPVD法により、セラミック皮膜を母材温度450~1200°Cで形成する。

【0012】その際に、超硬合金母材から炭化タングステン皮膜中に深さ5μm以上のコバルトの拡散浸透を得るために、炭化タングステン皮膜を有する超硬合金母材が950~1200°Cで5時間以上加熱されることが必要である。この加熱条件を満たすためには、セラミック皮膜の形成に先立って又はセラミック皮膜の形成後に950~1200°Cで5時間以上の拡散焼純を行うか、又はセラミック皮膜の成膜時の熱履歴を利用して母材温度950~1200°C及び成膜時間5時間以上の条件で成膜すれば良いが、拡散焼純とセラミック皮膜の成膜時の加熱の両方により合計で950~1200°Cで5時間以上の加熱条件を達成しても良い。

#### 【0013】

【作用】本発明においては、従来から被覆超硬合金に用いられているセラミック皮膜、例えばTiC、TiN、Ti(CN)、HfN、HfC、Hf(CN)、ZrN、ZrC、Zr(CN)、TiBN、Al<sub>2</sub>O<sub>3</sub>、HfO<sub>2</sub>、ZrO<sub>2</sub>等の下地層として、セラミックの1種である炭化タングステン(WC)の厚膜を用い、更に超硬合金の結合相であるコバルトを母材からWC皮膜中に5μm以上の深さにわたって積極的に拡散浸透させることにより、被覆層の厚膜化にも拘らずWC皮膜の韌性が向上し且つ硬度の低下も殆ど起らないばかりか、母材との密着性も著しく改善されることが判明し、もって被覆超硬合金の耐摩耗性を著しく向上させることができた。

【0014】WC皮膜の膜厚は、切削工具や金型、治具等として使用される環境や設定された寿命、寸法精度等により左右されるが、一般的には5~100μmの範囲であることが好ましい。膜厚が5μm未満では、WC皮膜の形成及びCoの拡散による耐摩耗性向上の効果が殆どみられず、又100μmを越えるとWC皮膜が比較的脆くなり、被覆超硬合金の韌性が低下するだけでなく、成膜に長時間を要するため製造コストが増大するからである。

【0015】かかるWC皮膜の形成方法としては、タングステンの塩化物やカルボニルを用いた熱CVD法、金属タングステンを用いたイオンプレーティング法やスパッタリング法等のPVD法が考えられる。しかし、本発明では比較的厚いWC皮膜を得るために、経済的にも10μm/時以上の成膜速度が必要であるが、PVD法では高融点金属であるタングステンの供給速度を上げることが困難であるため、成膜速度はせいぜい1μm/時と極めて遅い。又、従来の熱CVD法では、原料であるタングステンの塩化物やカルボニルの蒸気圧が低いため、5μm/時以上の成膜速度を得ることは難しい。

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【0016】そこで検討の結果、タンゲステンのフッ化物（例えばWF<sub>6</sub>）を用いた熱CVD法によれば、フッ化物ガスの高速供給が可能であり、これをC<sub>3</sub>H<sub>8</sub>やC<sub>6</sub>H<sub>6</sub>等の炭化水素ガス及び水素ガスと反応させることで、WC皮膜を極めて高速で成膜できることが判った。ただし、超硬合金の母材温度が500°C未満では、10μm/時以上の成膜速度を達成できないばかりか、得られるWC皮膜中の炭素含有率が低く、皮膜構成相がW<sub>3</sub>Cの単一相となるため、極めて脆いWC皮膜しか得られない。逆に、母材温度が900°Cを越えると、原料ガスが気相中で反応してしまい、粉末状の生成物しか得られない。

【0017】次に、このWC皮膜の上に、TiC、TiN、Ti(CN)、HfN、HfC、Hf(CN)、ZrN、ZrC、Zr(CN)、TiBN、Al<sub>2</sub>O<sub>3</sub>、HfO<sub>2</sub>、ZrO<sub>2</sub>等のセラミック皮膜を被覆する。その形成方法としては、熱CVD法、プラズマCVD法、MO-CVD法等のCVD法や、イオンプレーティング法等のPVD法を利用できるが、母材温度を450~1200°Cにする必要がある。その理由は、母材温度が450°C未満ではセラミック皮膜の密着性が低く、後工程での熱履歴に耐えられずに皮膜が剥離する危険があり、一方1200°Cを越えると母材である超硬合金の組織に変化が生じ、本来の超硬合金の性能が損なわれるからである。

【0018】更に本発明においては、超硬合金の結合相をなすCoが、母材からWC皮膜中に深さ5μm以上拡散浸透していることを要するが、そのためには950~1200°Cで5時間以上の加熱処理が必要であることが判明した。温度が950°C未満又は加熱時間が5時間未満では、CoがWC皮膜中に5μm以上の深さに拡散されず、又温度が1200°Cを越えると、母材である超硬合金の組織に変化が生じ、本来の超硬合金の性能が損なわれる。

【0019】このCoの拡散浸透を得るための加熱方法としては、①セラミック皮膜の形成に先立って又はセラミック皮膜の形成後に950~1200°Cで5時間以上の拡散焼純を行うか、又は②セラミック皮膜の成膜時の熱履歴を利用して、母材温度950~1200°Cで5時間以上かけて成膜する方法があるが、③上記拡散焼純とセラミック皮膜の成膜時の加熱の両方を合わせて上記950~1200°Cで5時間以上の加熱条件を満たすようにしても良い。

【0020】以上のWC皮膜の形成、拡散焼純、及びセラミック皮膜の形成の各工程は、それぞれ別の成膜装置や熱処理炉で行っても良いが、できれば同一の成膜装置内で大気にさらすことなく、連続的に処理することが好ましい。被処理物が移動の際に大気に触れると、表面が大気中の酸素や水分によって汚染され、後工程の処理に悪影響を及ぼす恐れがあるからである。又、各工程毎に別々の装置を使用すると、装置から装置への移動等の段

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取り時間が余分に発生し、製造コストを上昇させる原因にもなる。

【0021】しかしながら、セラミック皮膜の形成をイオンプレーティング法等のPVD法により実施する場合には、WC皮膜の形成がCVD法によるため必ずしも同一装置を使用できないので、WC皮膜の成膜及び必要に応じて拡散焼純をCVD法の成膜装置内で行い、母材を大気中に取り出した後、洗浄してからPVD法の成膜装置内に取付てセラミック皮膜を形成することが好ましい。

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【実施例】

実施例1

WC: 85重量%、Co: 10重量%、及びTiC: 5重量%からなる組成を持つ超硬合金工具を、耐熱合金製の成膜装置内部に設置し、次の反応条件の熱CVD法により、

(1)反応ガス条件: WF<sub>6</sub> 1モル%

C<sub>6</sub>H<sub>6</sub> 5モル%

20 H<sub>2</sub> 10モル%

(2)反応ガス流量: 1.6リットル/分

(3)母材温度: 800°C

(4)反応時間: 30分

表面にWC皮膜を形成した。

【0023】得られたWC皮膜は、X線回折によりα-WCで構成されていることが確認できた。又、WC皮膜の膜厚は7μmであり、成膜速度は14μm/時であることが分かった。このWC皮膜の断面硬度をヌープ硬度計(荷重50g)で測定したところ、WC皮膜の硬度として約2400kg/mm<sup>2</sup>の値が得られた。更に、WC皮膜の密着強度を引張式密着強度測定機を用いて評価したところ、25N(ニュートン)で皮膜の剥離が生じた。

【0024】このWC被覆超硬合金工具を、再度同じ成膜装置内部に設置し、通常の熱CVD法により、母材温度980°Cのもとで反応時間3時間を要してTiC皮膜を形成し、更にその上に母材温度1000°Cのもとで反応時間5時間を要してAl<sub>2</sub>O<sub>3</sub>皮膜を形成した(本発明例1)。得られた本発明例1の被覆超硬合金工具断面の金属組織の写真を図1に示した。この断面観察により、TiC皮膜とAl<sub>2</sub>O<sub>3</sub>皮膜の合計膜厚は6μmであつて、母材からWC皮膜中にほぼ7μmの深さまでCoが拡散浸透していることが確認できた。

【0025】又、皮膜の密着強度を上記と同様に測定したところ、WC皮膜とTiC皮膜との界面での剥離は認められず、WC皮膜と母材との界面での剥離は9.5Nで発生し、WC皮膜のみの場合よりも遙かに密着強度が向上していることが分かった。更に、上記と同じヌープ硬度計で測定した被覆超硬合金工具の厚さ方向の断面硬度を図2に示した。

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【0026】比較のために、上記と同様にWC皮膜を形成したWC被覆超硬合金工具の表面に、TiC皮膜とAl<sub>2</sub>O<sub>3</sub>皮膜をプラズマCVD法を用いて母材温度900°Cで形成した（比較例1）。得られた比較例1の被覆超硬合金工具の断面を観察したところ、TiC皮膜とAl<sub>2</sub>O<sub>3</sub>皮膜の合計膜厚は5μmであり、母材とWC皮膜との間でCoの拡散は全く認められなかった。又、上記と同様に皮膜の密着強度を測定したところ、母材とWC皮膜との界面での剥離は30Nでおこり、密着強度は本発明例1に比べて極めて低かった。

## 【0027】実施例2

上記実施例1と同様にWC皮膜（膜厚7μm）を形成したWC被覆超硬合金工具を、1050°Cで5時間焼純した後、このWC皮膜の上に下記のセラミック皮膜を形成し、本発明例2～5の被覆超硬合金工具を得た；  
本発明例2：TiC皮膜とTiBN皮膜とAl<sub>2</sub>O<sub>3</sub>皮膜を積層した合計膜厚6μmのセラミック皮膜（プラズマCVD法；母材温度900°C）

本発明例3：HfO<sub>2</sub>皮膜とAl<sub>2</sub>O<sub>3</sub>皮膜を積層した合計膜厚7μmのセラミック皮膜（金属アルコキシドを用いたMO-CVD法；母材温度700°C）

本発明例4：HfN皮膜とHfC皮膜を積層した合計膜厚6μmのセラミック皮膜（イオンプレーティング法；母材温度600°C）

本発明例5：ZrN皮膜とZr(CN)皮膜とZrC皮膜を積層した合計膜厚7μmのセラミック皮膜（イオンプレーティング法；母材温度600°C）

【0028】本発明例2～5の各被覆超硬合金工具の断面を観察したところ、いずれも母材から膜厚7μmのWC皮膜中に深さ6μmにわたってCoが拡散しており、WC皮膜の密着強度は本発明例2で95N、本発明例3\*

10 工具断面を観察したところ、母材からWC皮膜へのCoの拡散浸透はわずか2μm程度に止まり、WC皮膜の密着強度は40Nであった。

## 【0030】実施例3

上記実施例1及び実施例2で作製した本発明例1～5と、比較例1～2について、下記条件による切削試験を行った。尚、WC皮膜を形成しない以外は実施例1と同じにして、超硬合金工具表面に合計膜厚6μmのTiC皮膜とAl<sub>2</sub>O<sub>3</sub>皮膜を形成した被覆超硬合金工具（比較例3）についても、同様に下記条件による切削試験を行った。

## 【0031】

切削条件：被削材 SCM435

切削速度 250m/min

送り 0.3mm/rev.

切り込み 2mm

切削時間 20分

【0032】上記切削試験によりフランク摩耗及びクレータ摩耗を測定し、結果を各被覆超硬合金工具の積層皮膜の構成、WC皮膜中のCo拡散浸透の深さと共に、下記表1に示した；

## 【表1】

工具試料	積層皮膜の構成	Co拡散深さ (μm)	フランク 摩耗(mm)	クレータ 摩耗(μm)
本発明例1	WC-TiC-Al <sub>2</sub> O <sub>3</sub>	7	0.09	11
本発明例2	WC-TiC-TiBN-Al <sub>2</sub> O <sub>3</sub>	6	0.10	12
本発明例3	WC-HfO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	6	0.12	15
本発明例4	WC-HfN-HfC	6	0.11	14
本発明例5	WC-ZrN-Zr(CN)-ZrC	6	0.12	13
比較例1	WC-TiC-Al <sub>2</sub> O <sub>3</sub>	0	欠損	欠損
比較例2	WC-TiC-TiBN-Al <sub>2</sub> O <sub>3</sub>	2	0.32(剥離)	20
比較例3	TiC-Al <sub>2</sub> O <sub>3</sub>	-	0.28	25

(注) 比較例2では切削中に皮膜の一部に剥離が発生した。

【0033】上記表1の結果から、WC皮膜中のCoの拡散浸透が少ない比較例1と2、及びWC皮膜を有しない比較例3に比べて、本発明例の被覆超硬合金工具はいずれも優れた耐摩耗性を示し、Coの拡散したWC皮膜の耐摩耗性向上に与える効果が顕著であることが明白である。又、WC皮膜へのCoの拡散については、拡散の深さを支配する拡散焼純やセラミック皮膜成膜時の温度と時間の履歴が重要であることが判る。

※50 順次積層してセラミック皮膜を形成した。

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\*で93N、本発明例4で92N、及び本発明例5で94Nと、いずれも実施例1で求めたこのWC皮膜単独での密着強度25Nより大幅に改善されていた。

【0029】比較のために、同じWC皮膜（膜厚7μm）を形成したWC被覆超硬合金工具を、1000°Cで2時間焼純した後、このWC皮膜の上にTiC皮膜、TiBN皮膜、及びAl<sub>2</sub>O<sub>3</sub>皮膜を積層した合計膜厚6μmのセラミック皮膜を、プラズマCVD法を用いて母材温度900°Cで形成した（比較例2）。この比較例2の

10 工具断面を観察したところ、母材からWC皮膜へのCoの拡散浸透はわずか2μm程度に止まり、WC皮膜の密着強度は40Nであった。

## 【0030】実施例3

上記実施例1及び実施例2で作製した本発明例1～5と、比較例1～2について、下記条件による切削試験を行った。尚、WC皮膜を形成しない以外は実施例1と同じにして、超硬合金工具表面に合計膜厚6μmのTiC皮膜とAl<sub>2</sub>O<sub>3</sub>皮膜を形成した被覆超硬合金工具（比較例3）についても、同様に下記条件による切削試験を行った。

## 【0031】

切削条件：被削材 SCM435

切削速度 250m/min

送り 0.3mm/rev.

切り込み 2mm

切削時間 20分

【0032】上記切削試験によりフランク摩耗及びクレータ摩耗を測定し、結果を各被覆超硬合金工具の積層皮膜の構成、WC皮膜中のCo拡散浸透の深さと共に、下記表1に示した；

## 【表1】

工具試料	積層皮膜の構成	Co拡散深さ (μm)	フランク 摩耗(mm)	クレータ 摩耗(μm)
本発明例1	WC-TiC-Al <sub>2</sub> O <sub>3</sub>	7	0.09	11
本発明例2	WC-TiC-TiBN-Al <sub>2</sub> O <sub>3</sub>	6	0.10	12
本発明例3	WC-HfO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	6	0.12	15
本発明例4	WC-HfN-HfC	6	0.11	14
本発明例5	WC-ZrN-Zr(CN)-ZrC	6	0.12	13
比較例1	WC-TiC-Al <sub>2</sub> O <sub>3</sub>	0	欠損	欠損
比較例2	WC-TiC-TiBN-Al <sub>2</sub> O <sub>3</sub>	2	0.32(剥離)	20
比較例3	TiC-Al <sub>2</sub> O <sub>3</sub>	-	0.28	25

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【0035】得られた本発明例の被覆超硬合金金型の断面を観察したところ、WC皮膜の膜厚が $5\mu\text{m}$ 、及びセラミック皮膜の合計膜厚が $6\mu\text{m}$ であり、超硬合金の結合相であるCoが母材である超硬合金からWC皮膜中に深さ $8\mu\text{m}$ にわたり拡散浸透していることが確認できた。

【0036】比較のために、WC皮膜を設けることなく、同じ超硬合金金型の表面にTiC皮膜+Ti(CN)皮膜+TiN皮膜を積層してなるセラミック皮膜を直接形成した金型を作製した。この比較例と上記本発明例の被覆超硬合金金型を用いて、自動車部品の冷間鍛造を実施し、各金型の寿命評価を行った。その結果、本発明例の金型は30万ショットで寿命に達したのに対し、比較例の金型はわずか5万ショットと極めて短い寿命であった。又、損傷した金型を観察すると、損傷の最も激しい金型先端のコーナー部において、本発明例の金型ではWC皮膜が残存していたのに対して、比較例の金型では下地の超硬合金が露出していた。

#### 【0037】実施例5

WC: 90重量%とCo: 10重量%からなる超硬合金製メカニカルシールの表面に、実施例1と同様の方法により膜厚 $80\mu\text{m}$ のWC皮膜を形成し、次に $1200^\circ\text{C}$ で6時間の拡散焼純を施した。その後、このWC皮膜の上に同じ成膜装置内で、プラズマCVD法により母材温度 $700^\circ\text{C}$ で膜厚 $5\mu\text{m}$ のTiN皮膜を形成した。

【0038】この本発明例の被覆超硬合金製メカニカルシールの断面を観察したところ、超硬合金の結合相であるCoが、母材である超硬合金からWC皮膜中に深さ $20\mu\text{m}$ にわたり拡散浸透していた。比較のために、WC

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皮膜を設けることなく、同じ超硬合金製メカニカルシールの表面にTiN皮膜を直接形成したメカニカルシールを作製した。これらの被覆超硬合金製メカニカルシールを、同じ形式のスラリー用ポンプに組み付けて、耐久性評価試験を実施した。

【0039】その結果、本発明例では2万時間経過後も焼き付きや摩耗が生ぜず、なお問題なく使用できたのに對して、比較例では5000時間でシール部からスラリーの漏れが生じて寿命に達した。試験後、メカニカルシールを調査したところ、比較例のものはTiN皮膜が摩耗して下地の超硬合金が露出していただけでなく、超硬合金の腐食も観察され、深さ $100\mu\text{m}$ を越える摩耗痕も認められたが、本発明例のものはWC皮膜が $5\mu\text{m}$ の深さまで摩耗しているだけで、腐食の兆候は全く認められなかった。

#### 【0040】

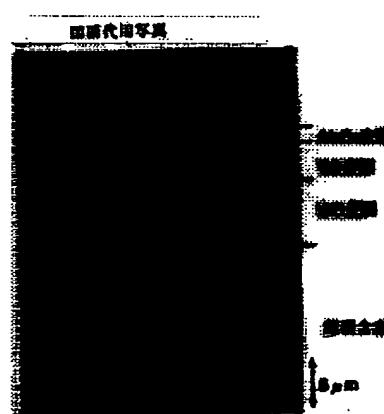
【発明の効果】本発明によれば、被覆層の厚膜化によっても韌性の低下を招かず且つ被覆層と超硬合金母材との密着性に優れ、切削工具や金型、耐摩具、機械部品、構造材料等として使用したとき、従来を遥かに越える寿命を達成し得るのみならず、従来使用できなかつた過酷な条件下での使用も可能な、新しい被覆超硬合金を提供することができる。

#### 【図面の簡単な説明】

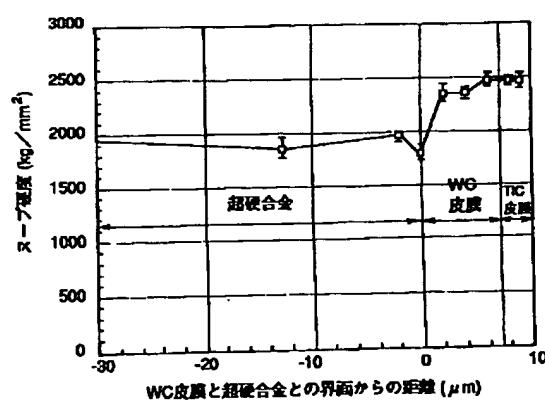
【図1】実施例1で作製した本発明例の被覆超硬合金工具における断面の金属組織を示す写真である。

【図2】実施例1で作製した本発明例の被覆超硬合金工具の厚さ方向における断面硬度を示すグラフである。

【図1】



【図2】



フロントページの続き

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